



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/US98/26137 <b>(22) International Filing Date:</b> 9 December 1998 (09.12.98)  <b>(30) Priority Data:</b> 09/000,988 30 December 1997 (30.12.97) US  <b>(71) Applicant:</b> CHEVRON CHEMICAL COMPANY LLC [US/US]; 555 Market Street, San Francisco, CA 94105 (US).  <b>(72) Inventor:</b> GEE, Jeffery, C.; 2062 Fir Springs, Kingwood, TX 77339 (US).  <b>(74) Agents:</b> HAYMOND, W., Bradley et al.; Chevron Corporation, Law Dept., P.O. Box 7141, San Francisco, CA 94120-7141 (US).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> INVERT EMULSION DRILLING FLUID CONTAINING MIXTURES OF SECONDARY ESTERS OBTAINED BY CONVERSION OF OLEFINS, AND PREPARATION THEREOF  <b>(57) Abstract</b>  Preparation of invert drilling muds containing a mixture of secondary esters, the process involving the addition of one or more C <sub>1</sub> -C <sub>5</sub> carboxylic acids and one or more C <sub>3</sub> -C <sub>22</sub> olefins in the presence of an acid catalyst.		

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1 Invert emulsion drilling fluid containing mixtures of secondary esters  
2 obtained by conversion of olefins, and preparation thereof.

3  
4 FIELD OF THE INVENTION

5  
6 The invention relates to a process for combining an olefin and a carboxylic  
7 acid to produce a mixture containing secondary esters; the mixture of esters  
8 produced by the process and the use of the mixture of esters.

9  
10 BACKGROUND OF THE INVENTION

11  
12 It is known that carboxylic acids can be added to olefins to produce  
13 secondary esters (meaning an ester in which the carbon on the alkyl chain to  
14 which the carboxylate moiety is attached is a secondary carbon, i.e., one that  
15 is covalently bound to two other carbon atoms, rather than a primary or  
16 tertiary carbon, which are covalently bound to one or three carbon atoms,  
17 respectively). These methods generally involve reaction of a low molecular  
18 weight olefin with a high molecular weight carboxylic acid to produce  
19 secondary esters.

20  
21 Catalysts known to be effective in such esterification reactions can be in the  
22 form of metallosilicates, especially aluminum silicates (such as zeolites or  
23 zeolite mordenites) having exchangeable cations and hydrogen  
24 ion-exchanged, layered clays. For esterification reactions, these catalysts are  
25 often used with a strong acid added to them.

26  
27 With hydrogen ion-exchanged, layered clays, it is also known that if the  
28 exchangeable cation in the layered clay is a metal cation, there is no need for  
29 strong acids to be added to the catalyst. The absence of strong acids renders  
30 the clays less corrosive and more readily separable from the reaction mixture.

31

1 Stabilized pillared interlayered clay in which the pillars are formed after  
2 exchanging the natural cations of the clay with more suitable cations are  
3 known to be effective for catalyzing the esterification reaction of olefins and  
4 carboxylic acids.

5

6 It is also known that monocarboxylic acid methyl esters can be used as the  
7 continuous phase or part of the continuous phase in invert drilling muds.

8

9 The present invention relates to an esterification reaction of olefins and  
10 carboxylic acids which results in a significant decrease in oligomerization and  
11 utilizes a catalyst which is relatively easy to prepare and is relatively long-  
12 lasting in its effectiveness. The present invention also relates to the product  
13 of this esterification reaction which can be used as a component of a drilling  
14 fluid.

15

## 16 SUMMARY OF THE INVENTION

17

18 An object of the present invention is to provide an invert emulsion drilling fluid  
19 comprising:

20

21 (a) a continuous phase comprising a mixture of secondary esters selected  
22 from the group consisting of propylcarboxylates, butylcarboxylates,  
23 pentylcarboxylates, hexylcarboxylates, heptylcarboxylates,  
24 octylcarboxylates, nonylcarboxylates, decylcarboxylates,  
25 undecylcarboxylates, dodecylcarboxylates, tridecylcarboxylates,  
26 tetradecylcarboxylates, pentadecylcarboxylates, hexadecylcarboxylates,  
27 heptadecylcarboxylates, octadecylcarboxylates, nonadecylcarboxylates,  
28 eicosylcarboxylates, uneicocarboxylates, doeicosylcarboxylates and  
29 isomers and mixtures thereof, wherein the secondary esters each have  
30 a carboxylate moiety with from one to five carbon atoms;

31

1 (b) a weight material; and

2

3 (c) water.

4

5 Still another object of the present invention is to provide a method of making  
6 secondary esters comprising combining carboxylic acids having from one to  
7 five carbon atoms or isomers or mixtures thereof with olefins selected from  
8 the group consisting of propene, butene, pentene, hexene, heptene, octene,  
9 nonene, decene, undecene, dodecene, tridecene, tetradecene, pentadecene,  
10 hexadecene, heptadecene, octadecene, nonadecene, eicosene, uneicosene,  
11 doeicosene and isomers and mixtures thereof in the presence of an acid  
12 catalyst.

13

14 Yet another object of the present invention is to provide a method of using a  
15 mixture of secondary esters as the continuous phase or part of the  
16 continuous phase of an invert drilling fluid, the mixture being produced by a  
17 method comprising the step of combining carboxylic acids having from one to  
18 five carbon atoms or isomers or mixtures thereof with olefins selected from  
19 the group consisting of propene, butene, pentene, hexene, heptene, octene,  
20 nonene, decene, undecene, dodecene, tridecene, tetradecene, pentadecene,  
21 hexadecene, heptadecene, octadecene, nonadecene, eicosene, uneicosene,  
22 doeicosene and isomers and mixtures thereof in the presence of an acid  
23 catalyst to make secondary esters.

24 Still another object of the present invention is to provide a method of using a  
25 mixture of secondary esters as an additive to water based drilling muds, the  
26 mixture being produced by a method comprising the step of combining  
27 carboxylic acids having from one to five carbon atoms or isomers or mixtures  
28 thereof with olefins selected from the group consisting of propene, butene,  
29 pentene, hexene, heptene, octene, nonene, decene, undecene, dodecene,  
30 tridecene, tetradecene, pentadecene, hexadecene, heptadecene,  
31 octadecene, nonadecene, eicosene, uneicosene, doeicosene and isomers

1 and mixtures thereof in the presence of an acid catalyst to make secondary  
2 esters.

3

4

#### DESCRIPTION OF THE DRAWINGS

5

6 Figure 1 is a diagram of a continuous unit used to produce mixtures of  
7 secondary esters.

8

9 Figure 2 is a GC/FID chromatogram for a product mixture obtained from the  
10 unit when the unit was operating at about 0.65 WHSV and 140°C as  
11 described in Example 2.

12

13 Figure 3 is a GC/FID chromatogram for a product mixture obtained in a batch  
14 reactor when the reactor was operating for about 5 hours at 120°C as  
15 described in Example 3.

16

17

#### DETAILED DESCRIPTION OF THE INVENTION

18

19 This invention relates to the use of an acid catalyst, preferably a dry  
20 (extremely low moisture) acid washed natural clay, to catalyze the addition of  
21 a C<sub>1</sub>-C<sub>5</sub> carboxylic acid to an olefin. The process can utilize one acid or a  
22 mixture of acids, and it can utilize one olefin or a mixture of olefins. The  
23 process can proceed in batch or continuous mode and operates at 60-300°C.  
24 In a continuous mode, the flow rate is generally 0.1-5 WHSV. Some of the  
25 most surprising attributes of this invention are (1) that the catalyst must be  
26 nearly free of water in order for the esterification reaction to proceed; and  
27 (2) that olefin oligomerization is almost eliminated, as long as the  
28 concentration of carboxylic acid in the feedstock mixture is kept above about  
29 3 wt. %.

30

1 As a hydrophobic synthetic fluid with a pour point below  $-10^{\circ}\text{C}$ , a flash point  
2 above about  $120^{\circ}\text{C}$ , and a molecular weight near that of a  $\text{C}_{14}\text{-C}_{20}$   
3 hydrocarbon, these synthetic mixtures would function well as the continuous  
4 phase or part of the continuous phase of an invert mud. Because these  
5 mixtures are mixtures of esters rather than hydrocarbons, they would  
6 biodegrade more rapidly than do synthetic hydrocarbons.

7  
8 Another advantage that this invention gives over esters currently used in the  
9 drilling industry is that from it can be produced a suitable ester mixture having  
10 a lower viscosity than esters currently in use. Currently used esters derive  
11 from natural fatty acids, which are typically  $\text{C}_{12}$  or heavier acids. When  
12 combined with a branched  $\text{C}_8$  or heavier alcohol, which is the conventional  
13 practice used to get an ester with a sufficiently low pour point, the resulting  
14 ester is more viscous than the ones that can be achieved with the present  
15 invention.

16  
17 The following non-limiting examples show various aspects of various  
18 embodiments of the present invention.

19

## 20 EXAMPLES

21

### 22 Example 1

#### 23 Synthesis of $\text{C}_{14}$ Propionates with F-25

24

25 F-25 (Engelhard) was dried in a vacuum oven overnight at about  $200^{\circ}\text{C}$  to  
26 remove water. The dried clay granules were packed into a fixed bed, and a  
27 mixture that was 50 mole % propionic acid and 50 mole % commercial  
28 1-tetradecene was passed over the bed at a temperature of  $140^{\circ}\text{C}$  and a flow  
29 rate of 0.5 WHSV. By GC/FID analysis, the effluent contained about 20%  
30 secondary esters, about 10% propionic acid, about 70%  $\text{C}_{14}$  olefins, and less  
31 than 1%  $\text{C}_{14}$  oligomers. The single most abundant ester in the mixture was



1 2-tetradecyl propionate, followed by 3-tetradecyl propionate, followed by  
2 4-tetradecyl propionate, followed by 5-, 6- and 7-tetradecyl propionate. The  
3 C<sub>14</sub> olefins in the effluent were about 70% linear internal olefins and about  
4 30% alpha olefins. The unreacted acid and olefins were separated from the  
5 esters by distillation and were suitable for recycling.

6

7

### Example 2

8

#### Synthesis of C<sub>14</sub> Propionates with F-25

9

10 F-25 (Engelhard) was dried and packed into a fixed bed as in Example 1. A  
11 mixture that was 50 mole % propionic acid and 50 mole % commercial  
12 1-tetradecene was passed over the bed at a temperature of 140°C and a flow  
13 rate of 0.65 WHSV. The chromatogram of Figure 2 shows the peaks for  
14 residual propionic acid and tetradecenes remaining as well as the peaks for  
15 the secondary esters formed from tetradecenes and propionic acid formed.  
16 By GC/FID analysis, the effluent contained about 9% propionic acid, about  
17 73% tetradecenes, and about 15% secondary esters. Of particular note is the  
18 nearly complete absence of peaks for olefin dimers, which, by GC/FID, make  
19 up only about 1.8% of the product mixture.

20

21

### Example 3

22

#### Treatment of 1-Dodecene over Filtrol 105

23

24 As a comparison to the results of Example 2, Filtrol 105 (Engelhard) was  
25 dried as in Examples 1 and 2, then added to a batch reactor. A sample of  
26 1-dodecene was stirred and heated over the catalyst at 120°C for about  
27 5 hours. By GC/FID analysis, the effluent contained about 34% C<sub>12</sub> olefin  
28 monomer, 46% dimer and 20% trimer. In comparing these results with  
29 Examples 1 and 2, it can be seen that the presence of propionic acid,  
30 especially in an amount greater than about 3% propionic acid in the feed



1 stream, clearly keeps the level of dimer below 5%. The chromatogram of  
2 Figure 3 shows the peaks for the C<sub>12</sub> oligomers.

3

4

#### Example 4

5

#### Stopping Oligomerization Reaction with Propionic Acid

6

7 About 598 g of a mixture that was 67 mole % 1-tetradecene and 33 mole %  
8 propionic acid was heated and stirred at 140°C in a batch reactor with 50 g of  
9 dry F-25 (Engelhard). After 6.5 hours, the level of secondary esters peaked  
10 at about 20% by GC/FID, and olefin oligomers accounted for 3% of the  
11 reaction mixture. Instead of remaining steady, the ester level then began to  
12 decline, and there was a rapid increase in the amount of olefin oligomer. For  
13 the first seven hours of reaction, the propionic acid was >3% (by GC/FID) of  
14 the reaction mixture. Once the propionic acid dropped to <3% (by GC/FID) of  
15 the reaction mixture, the level of olefin oligomer began to increase rapidly.

16

#### Example 5

17

#### C<sub>14</sub> Propionates Evaluated as Base Fluid for Invert Drilling Emulsion

18

19 The suitability of the C<sub>14</sub> propionates for use in invert drilling fluids was  
20 evaluated. The invert emulsion was prepared by combining most of the  
21 components with the base fluid and mixing for 30 minutes at 120°F using a  
22 Gifford Wood homogenizer. The ingredients were added in the order listed in  
23 the table below, but the last three were not added during the 30-minute  
24 homogenizer cycle. First, the slurry from the homogenizer was transferred to  
25 a dispersator, and then the barite, drilling solids, and CaCl<sub>2</sub> were added, and  
26 the mixture was stirred for 30 minutes. Rheological properties of the resulting  
27 drilling fluid were determined at 120°F, before and after hot-rolling the  
28 emulsion for 16 hours at 150°F.

29

Component	Amount
C <sub>14</sub> Propionates	200.55 ml
Water	37.1 ml
Organoclay Viscosifier	3.0 g
Emulsion stabilizer	8.0 g
Emulsifier	4.0 g
Lime	3.0 g
Fluid loss additive	10.0 g
Rheological Modifier	0.5 g
Barite	334.0 g
Simulated drill solids	20.0 g
CaCl <sub>2</sub>	13.1 g

1

2 The drilling fluid showed the following rheological results at 120°F:

3

Parameter	Before hot rolling	After hot rolling
Fann Dial Reading @ 600 rpm	81	89
Fann Dial Reading @ 300 rpm	49	54
Fann Dial Reading @ 200 rpm	37	41
Fann Dial Reading @ 100 rpm	25	28
Fann Dial Reading @ 6 rpm	11	11
Fann Dial Reading @ 3 rpm	10	10
Plastic Viscosity @ 120°F, cps	32	35
Yield Point, lb/100 sq ft	17	19
10 s gel strength, lb/100 sq ft	16	16
10 m gel strength, lb/100 sq ft	22	27
Electrical stability @ 120°F	1328	1416
Oil mud alkalinity (Pom)	1.485	--
Excess lime, lb/bbl	1.93	--
HTHP filtrate @ 300°F, 500 psi	--	3.6

Parameter	Before hot rolling	After hot rolling
Water, ml	--	0.0
Cake thickness, HTHP, 32 <sup>nd</sup>	--	2

1

2 Values of some physical properties of the C<sub>14</sub> propionates were:

3

kinematic viscosity @ 40°C	4.25 cSt
kinematic viscosity @ 100°C	1.56 cSt
flash point (°C)	156
pour point (°C)	-29
specific gravity @ 60°F	0.86

4

5

#### Example 6

6

#### Mysid Shrimp Toxicity Test

7

8 Additionally, the toxicity to mysid shrimp of the drilling fluid of Example 4 was  
9 evaluated according to the US EPA protocol in Appendix 3 of "Effluent  
10 Limitation Guidelines and New Source Performance Standards: Drilling  
11 Fluids Toxicity Test," Federal Register Vol. 50, No. 165, 34631-34636. For  
12 cuttings discharge, the drilling fluid must show an LC<sub>50</sub> toward mysid shrimp  
13 of at least 30,000 ppm. The drilling fluid prepared using the C<sub>14</sub> propionates  
14 had an LC<sub>50</sub> of  $\geq 1,000,000$  ppm, indicating the C<sub>14</sub> propionates make an  
15 extremely low toxicity drilling fluid.

16

17

#### Example 7

18

#### Synthesis of C<sub>12</sub> propionates with Dried F-25

19

20 A mixture that was 50 mole % propionic acid and 50 mole % commercial  
21 1-dodecene was passed over the same dried F-25 (Engelhard) catalyst as  
22 described in Examples 1 and 2. The flow rate was 0.35 WHSV, and the

-10-

1 temperature was 140°C. By GC/FID analysis, the effluent contained about  
2 20% secondary esters, about 10% propionic acid, about 70% C<sub>12</sub> olefins, and  
3 less than 1% C<sub>12</sub> oligomers. The single most abundant ester in the mixture  
4 was 2-dodecyl propionate, followed by 3-dodecyl propionate, followed by  
5 4-dodecyl propionate, followed by 5 & 6-dodecyl propionate. The unreacted  
6 acid and olefins were separated from the esters by distillation and were  
7 suitable for recycle.

8  
9 Values of some physical properties of the C<sub>12</sub> propionates were:

kinematic viscosity @ 40°C	3.05 cSt
kinematic viscosity @ 100°C	1.22 cSt
flash point (°C)	138
pour point (°C)	-62
specific gravity @ 60°F	0.86

11

### 12 Example 8

#### 13 Synthesis of C<sub>12</sub> Propionates with Amberlyst 15

14

15 A mixture containing 15 g propionic acid, 40 g 1-tetradecene, and 15 g of  
16 Amberlyst 15 (Rohm and Haas) was stirred and heated to 140°C. Within  
17 30 minutes, the mixture contained 20% tetradecyl propionates and <1% olefin  
18 oligomers by GC/FID. With additional reaction time, the oligomer content  
19 increased, and the ester level decreased.

20

### 21 Example 9

#### 22 Synthesis of C<sub>12</sub> Propionates with Amberlyst 15

23

24 A mixture containing 15 g propionic acid, 40 g 1-tetradecene, and 15 g of  
25 Amberlyst 15 (Rohm and Haas) was stirred and heated to 120°C. Within one  
26 hour, the mixture contained 31% tetradecyl propionates and <1% olefin

1 oligomers by GC/FID. With additional reaction time, the oligomer content  
2 increased, and the ester level decreased.

3

4

#### Example 10

5

#### Synthesis of C<sub>12</sub> Propionates with Amberlyst 15

6

7 A mixture containing 15 g propionic acid, 40 g 1-tetradecene, and 15 g of  
8 Amberlyst 15 (Rhom and Haas) was stirred and heated to 100°C. Within  
9 1.5 hours, the mixture contained 39% tetradecyl propionates and <1% olefin  
10 oligomers by GC/FID. With additional reaction time, the oligomer content  
11 increased, and the ester level decreased.

12

13

#### Example 11

14

#### Synthesis of C<sub>12</sub> Propionates with Amberlyst 15

15

16 A mixture containing 15 g propionic acid, 40 g 1-tetradecene, and 15 g of  
17 Amberlyst 15 (Rohm and Haas) was stirred and heated to 80°C. Within  
18 8 hours, the mixture contained 45% tetradecyl propionates and <1% olefin  
19 oligomers by GC/FID. With additional reaction time, the oligomer content  
20 increased, and the ester level decreased.

21

22

#### Example 12

23

#### Synthesis of C<sub>12</sub> Propionates with Undried F-25

24

25 A mixture containing 8.1 g 1-decene (1 eq), 17.5 g propionic acid (4 eq), and  
26 4.72 g commercial F-25 clay (Engelhard) was stirred and heated to 120°C.  
27 (The clay had not been oven dried after purchase.) The mixture refluxed and  
28 would not heat above 120°C. After 5 days, the mixture contained 6.5% esters  
29 by GC/FID. Then the condenser was removed, and vapor was allowed to  
30 leave the reaction vessel. Within 2 hours, the temperature had reached

-12-

1 140°C, and the mixture had reached 11% esters. About 12 hours later, the  
2 ester level was 23%.

3 Example 13

4 Synthesis of C<sub>14</sub> Propionates with Dried F-25

5  
6 A mixture containing 30.0 g 1-tetradecene (1 eq), 34.0 g propionic acid (3 eq),  
7 and 10.1 g of F-25 clay (Engelhard) (dried 24 hours in vacuum oven at  
8 200°C) was stirred and heated to 140°C. The mixture showed no signs of  
9 refluxing and easily reached 140°C. Within 20 hours, the mixture contained  
10 35% esters by GC/FID. The ester level remained at this level, even after  
11 stirring another 24 hours at the reaction temperature.

12  
13 Example 14

14 Synthesis of C<sub>14</sub> Propionates with Undried F-62

15  
16 A mixture containing 20.0 g 1-tetradecene (1 eq), 7.58 g propionic acid (1 eq),  
17 and 5.0 g F-62 extrudate (Engelhard) was stirred and heated to 120°C. The  
18 mixture refluxed and showed only traces of ester by GC/FID, even after  
19 20 hours of heating.

20  
21 Example 15

22 Synthesis of C<sub>14</sub> Propionates with Dried F-62

23  
24 A mixture containing 40.0 g 1-tetradecene (1 eq), 15.1 g propionic acid (1 eq),  
25 and 16.3 g F-62 extrudate (Engelhard) (which had heated in a vacuum oven  
26 at 200°C for 20 hours) was stirred and heated to 140°C. After 19 hours, the  
27 mixture contained 31% esters by GC/FID. Additional reaction time did not  
28 increase the amount of ester in the mixture.

29

-13-

1                                    Example 16

2                    Synthesis of C<sub>14</sub> Propionates from Isomerized C<sub>14</sub> and Dried Filtrol 105

3  
4    A mixture containing 30 g (1 eq) tetradecenes (obtained by thorough double  
5    bond isomerization of 1-tetradecene), 34 g (3 eq) propionic acid, and 10 g dry  
6    Filtrol 105 clay (Engelhard) (which had heated in a vacuum oven at 200°C for  
7    20 hours) was stirred and heated to 140°C. After 31 hours, the mixture  
8    contained 23% esters by GC/FID. The product esters from this process were  
9    the same ones obtained when 1-tetradecene was the starting olefin, but the  
10   distribution of propionate isomers was different for this mixture than for those  
11   obtained when 1-tetradecene was the starting olefin. There was about as  
12   much 7-tetradecyl propionate as 2-tetradecyl propionate in this mixture,  
13   showing a much more evenly distributed attachment position for the  
14   propionate group in this mixture than for the mixture obtained using  
15   1-tetradecene as the starting olefin.

16

17                                    Example 17

18                    Synthesis of C<sub>18</sub> Propionates Using Dried F-25

19

20   A mixture containing 664 g (1 eq) 1-octadecene, 195 g (1 eq) propionic acid,  
21   and 51 g dry F-25 (Engelhard) (which had heated in a vacuum oven at 200°C  
22   for 20 hours) was stirred and heated to 140°C. After 6 hours, the mixture  
23   contained 19% secondary esters by GC/FID.

24

25                                    Example 18

26                    C<sub>12</sub> Propionates Evaluated as Base Fluid for Invert Drilling Emulsion

27

28   A mud formulated using a mixture of dodecyl propionates as the base fluid  
29   had this composition:

30



-14-

Component	Amount
C <sub>12</sub> Propionates	200.55 ml
Water	37.1 ml
Organoclay Viscosifier	3.0 g
Emulsion stabilizer	8.0 g
Emulsifier	4.0 g
Lime	3.0 g
Fluid loss additive	10.0 g
Rheological Modifier	0.5 g
Barite	334.0 g
Simulated drill solids	20.0 g
CaCl <sub>2</sub>	13.1 g

1

2 The drilling fluid showed the following rheological measurements at 120°F:

3

Parameter	Before hot rolling	After hot rolling
Mud density, lb/gal	14.5	--
Fann Dial Reading @ 600 rpm	74	70
Fann Dial Reading @ 300 rpm	45	40
Fann Dial Reading @ 200 rpm	34	30
Fann Dial Reading @ 100 rpm	21	20
Fann Dial Reading @ 6 rpm	8	8
Fann Dial Reading @ 3 rpm	7	7
Plastic Viscosity @ 120°F, cps	29	30
Yield Point, lb/100 sq ft	16	10
10 s gel strength, lb/100 sq ft	11	10
10 m gel strength, lb/100 sq ft	13	13
Electrical stability @ 120°F	800	912
Oil mud alkalinity (Pom)	1.33	---
Excess lime, lb/bbl	1.73	---
HTHP filtrate @ 300°F, 500 psi	---	4.8
Water, ml	---	0.0
Cake thickness, HTHP, 32 <sup>nd</sup>	--	1

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1

2 Before hot rolling, the mud also showed these properties at 35°F:

3

Parameter	Before hot rolling
Mud density, lb/gal	14.5
Fann Dial Reading @ 600 rpm	238
Fann Dial Reading @ 300 rpm	130
Fann Dial Reading @ 200 rpm	92
Fann Dial Reading @ 100 rpm	50
Fann Dial Reading @ 6 rpm	10
Fann Dial Reading @ 3 rpm	8
Plastic Viscosity @ 120°F, cps	108
Yield Point, lb/100 sq ft	22
10 s gel strength, lb/100 sq ft	14
10 m gel strength, lb/100 sq ft	26

4

5 In the mysid shrimp test, this mud showed an LC<sub>50</sub> of  $\geq 1,000,000$  ppm SPP.

6

7 Values of some physical properties of the C<sub>12</sub> propionates were:

kinematic viscosity @ 40°C	3.05 cSt
kinematic viscosity @ 100°C	1.22 cSt
flash point (°C)	138
pour point (°C)	-62
specific gravity @ 60°F	0.86

8

9

#### Example 19

10 C<sub>12</sub>/C<sub>14</sub> Propionates Evaluated as Base Fluid for Invert Drilling Emulsion

11

12 A mud formulated using a mixture of dodecyl propionates (50 wt. %) and  
13 tetradecyl propionates (50 wt. %) as the base fluid had this composition:

1

Component	Amount
C <sub>12</sub> /C <sub>14</sub> Propionates (1:1)	200.55 ml
Water	37.1 ml
Organoclay Viscosifier	3.0 g
Emulsion stabilizer	8.0 g
Emulsifier	4.0 g
Lime	3.0 g
Fluid loss additive	10.0 g
Rheological Modifier	0.5 g
Barite	334.0 g
Simulated drill solids	20.0 g
CaCl <sub>2</sub>	13.1 g

2

3 The drilling fluid showed the following rheological measurements at 120°F:

4

Parameter	Before hot rolling	After hot rolling
Mud density, lb/gal	14.5	--
Fann Dial Reading @ 600 rpm	74	79
Fann Dial Reading @ 300 rpm	45	46
Fann Dial Reading @ 200 rpm	34	34
Fann Dial Reading @ 100 rpm	21	22
Fann Dial Reading @ 6 rpm	8	8
Fann Dial Reading @ 3 rpm	7	7
Plastic Viscosity @ 120°F, cps	32	33
Yield Point, lb/100 sq ft	13	13
10 s gel strength, lb/100 sq ft	12	11
10 m gel strength, lb/100 sq ft	19	15
Electrical stability @ 120°F	1086	1097
Oil mud alkalinity (Pom)	1.59	---
Excess lime, lb/bbl	2.07	---
HTHP filtrate @ 300°F, 500 psi	--	4.2
Water, ml	--	0.0

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Parameter	Before hot rolling	After hot rolling
Cake thickness, HTHP, 32 <sup>nd</sup>	--	1

1

2 Before hot rolling, the mud also showed these properties at 35°F:

3

Parameter	Before hot rolling
Mud density, lb/gal	14.5
Fann Dial Reading @ 600 rpm	262
Fann Dial Reading @ 300 rpm	142
Fann Dial Reading @ 200 rpm	100
Fann Dial Reading @ 100 rpm	56
Fann Dial Reading @ 6 rpm	10
Fann Dial Reading @ 3 rpm	8
Plastic Viscosity @ 120°F, cps	120
Yield Point, lb/100 sq ft	22
10 s gel strength, lb/100 sq ft	14
10 m gel strength, lb/100 sq ft	26

4

5 In the mysid shrimp test, this mud showed an LC<sub>50</sub> of  $\geq 1,000,000$  ppm SPP.

6

7

#### Example 20

8

#### Synthesis of C<sub>14</sub> Propionates Using H<sub>2</sub>SO<sub>4</sub>

9

10 A mixture containing 20 g (1 eq) 1-tetradecene, 7.6 g (1 eq) propionic acid,  
11 and 0.62 g concentrated sulfuric acid was stirred and heated to 115°C. After  
12 15 hours, the mixture contained 44 % secondary esters by GC/FID.

13

14 Although a few embodiments of the invention have been described in detail  
15 above, it will be appreciated by those skilled in the art that various  
16 modifications and alterations can be made to the particular embodiments

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- 1 shown without materially departing from the novel teachings and advantages
- 2 of the invention. Accordingly, it is to be understood that all such modifications
- 3 and alterations are included within the spirit and scope of the invention as
- 4 defined by the following claims.

1    WHAT IS CLAIMED IS:

2

3    1.    An invert emulsion drilling fluid comprising:

4           (a)   a continuous phase comprising a mixture of secondary esters  
5                selected from the group consisting of propylcarboxylates,  
6                butylcarboxylates, pentylcarboxylates, hexylcarboxylates,  
7                heptylcarboxylates, octylcarboxylates, nonylcarboxylates,  
8                decylcarboxylates, undecylcarboxylates, dodecylcarboxylates,  
9                tridecylcarboxylates, tetradecylcarboxylates,  
10              pentadecylcarboxylates, hexadecylcarboxylates,  
11              heptadecylcarboxylates, octadecylcarboxylates,  
12              nonadecylcarboxylates, eicosylcarboxylates, uneicocarboxylates,  
13              doeicosylcarboxylates and isomers and mixtures thereof, wherein  
14              the secondary esters each have a carboxylate moiety with from  
15              one to five carbon atoms;

16           (b)   a weight material; and

17           (c)   water.

18    2.    The invert emulsion drilling fluid according to claim 1 wherein the  
19           kinematic viscosity of the secondary ester mixture is between 1 and  
20           2 cSt when measured at 100°C, and wherein the pour point of the  
21           secondary ester mixture is below -10°C.

22    3.    The invert emulsion drilling fluid of claim 1 further comprising one or  
23           more additives selected from the group consisting of emulsifiers, wetting  
24           agents, viscosifiers, densifiers, and fluid-loss preventatives.

- 1     4.    A method of making an invert emulsion drilling fluid comprising:
- 2            (a)   combining carboxylic acids having from one to five carbon atoms  
3                   or isomers or mixtures thereof with olefins selected from the group  
4                   consisting of propene, butene, pentene, hexene, heptene, octene,  
5                   nonene, decene, undecene, dodecene, tridecene, tetradecene,  
6                   pentadecene, hexadecene, heptadecene, octadecene,  
7                   nonadecene, eicosene, uneicosene, doeicosene and isomers and  
8                   mixtures thereof in the presence of an acid catalyst to make  
9                   secondary esters; and
- 10           (b)   combining the secondary esters of step (a) with water, a weight  
11                   material and additives selected from the group consisting of  
12                   emulsifiers, wetting agents, viscosifiers, densifiers, and fluid-loss  
13                   preventatives.
- 14     5.    The method according to claim 4 wherein step (a) is conducted at a  
15           temperature of from 60 to 300°C.
- 16     6.    The method according to claim 4 wherein step (a) is conducted in a  
17           batch mode.
- 18     7.    The method according to claim 4 wherein step (a) is conducted in a  
19           continuous mode.
- 20     8.    The method according to claim 7 wherein the flow rate is from 0.1 to  
21           5 WHSV.
- 22     9.    The method according to claim 4 wherein the acid catalyst is an acid  
23           washed natural clay.



- 1    10.    The method according to claim 9 wherein the acid catalyst is  
2            substantially free of water.
- 3    11.    The method according to claim 4 wherein the carboxylic acids are  
4            greater than 5 weight % of the combined olefins and carboxylic acids in  
5            step (a).
- 6    12.    An invert emulsion drilling fluid produced by the method of claim 4.
- 7    13.    A method of using a mixture of secondary esters as a continuous phase  
8            or part of a continuous phase of an invert drilling fluid comprising the  
9            steps of:
- 10            (a)    combining carboxylic acids having from one to five carbon atoms  
11                    or isomers or mixtures thereof with olefins selected from the group  
12                    consisting of propene, butene, pentene, hexene, heptene, octene,  
13                    nonene, decene, undecene, dodecene, tridecene, tetradecene,  
14                    pentadecene, hexadecene, heptadecene, octadecene,  
15                    nonadecene, eicosene, uneicosene, doeicosene and isomers and  
16                    mixtures thereof in the presence of an acid catalyst to make the  
17                    mixture of secondary esters; and
- 18            (b)    adding the mixture to an invert drilling mud as the continuous  
19                    phase or part of the continuous phase of the invert drilling fluid.
- 20    14.    A method of using a mixture of secondary esters as an additive to water  
21            based drilling muds comprising the steps of:
- 22            (a)    combining carboxylic acids having from one to five carbon atoms  
23                    or isomers or mixtures thereof with olefins selected from the group  
24                    consisting of propene, butene, pentene, hexene, heptene, octene,  
25                    nonene, decene, undecene, dodecene, tridecene, tetradecene,

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- 1 pentadecene, hexadecene, heptadecene, octadecene,
- 2 nonadecene, eicosene, uneicosene, doeicosene and isomers and
- 3 mixtures thereof in the presence of an acid catalyst to make the
- 4 mixture of secondary esters; and
- 5 (b) adding the mixture to a water based drilling mud.

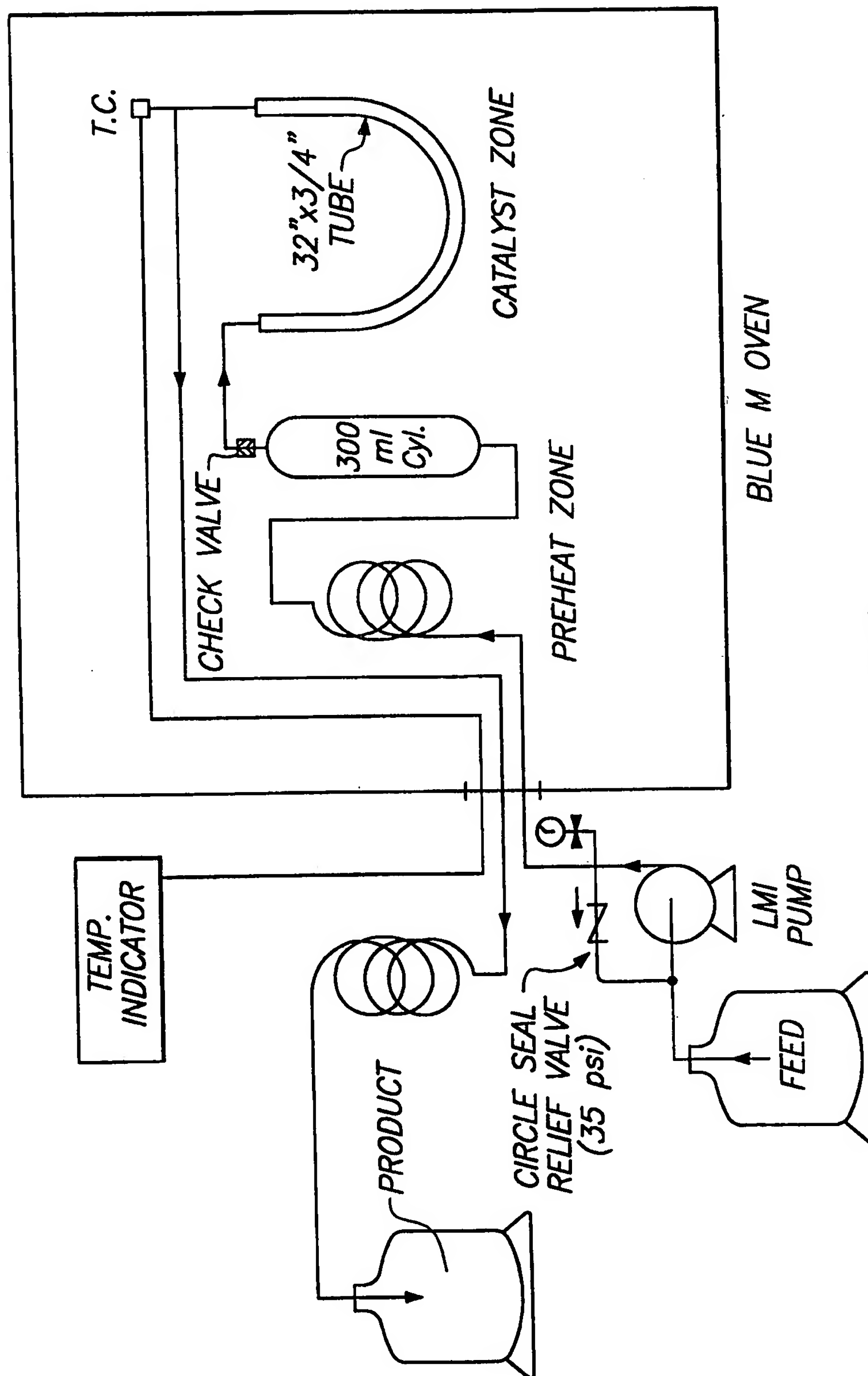


FIG. 1

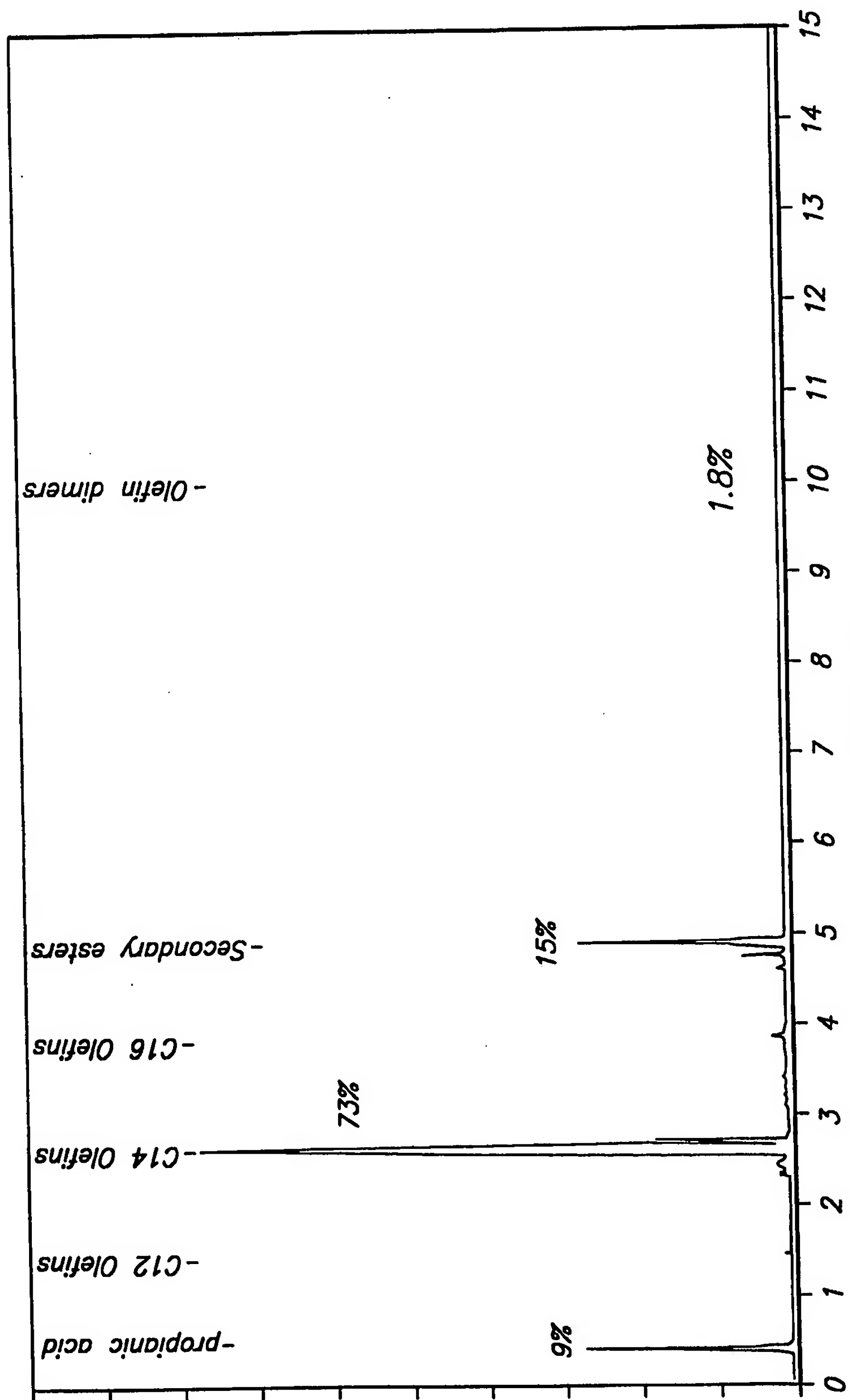


FIG. 2

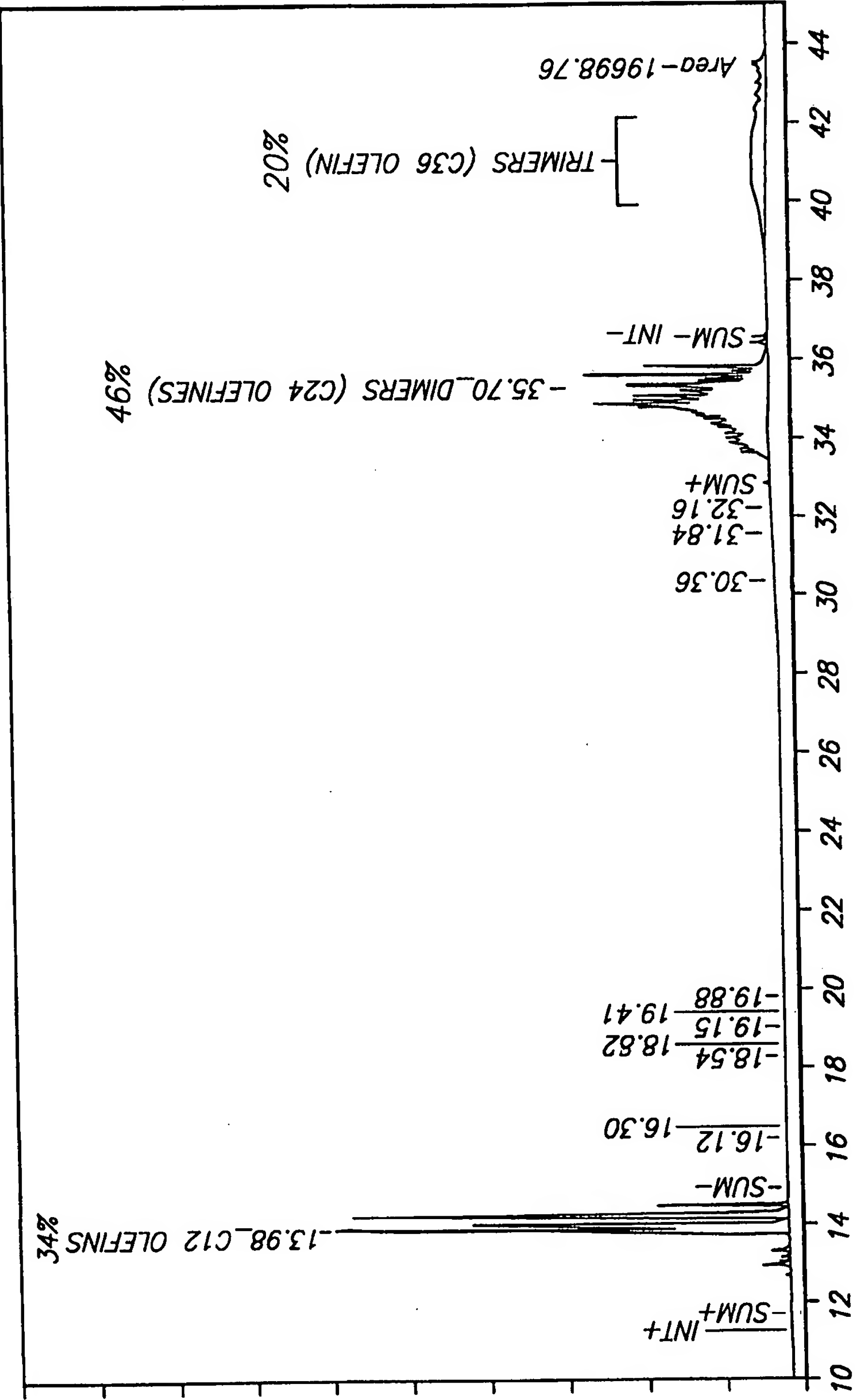


FIG. 3

# INTERNATIONAL SEARCH REPORT

Int. Application No

PCT/US 98/26137

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C09K7/06 C09K7/02 C09K7/00 C07C67/04

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C09K C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Y	EP 0 561 608 A (THE LUBRIZOL CORP.) 22 September 1993 see page 3, line 17 - line 56 see page 4, line 11 - line 16 see page 10, line 46 - page 12, line 21 see page 17, line 19 - line 40 ---	1,3,4, 12,14
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

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Int .tional Application No

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